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MARTIAN VOLATILES. COULD THEY BE STILL AT THE SURFACE? P. Jakeš, Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, Praha 2, Czech Republic.

The presence of volcanic rocks and the presence of water at the martian surface seem to be firmly established .The fate of martian volatiles remains mystery however. Loss to space and formation of cryosphere (formation of subsurface frozen layer) were advocated. Beforehand however vigorous isotopic exchange between volatiles and surface rocks have taken place [1].

Volcanos in Tharsis region, mineral and chemical composition of martian meteorites, composition of Viking and Mars Pathfinder sites [2], leave no doubt that volcanism has played an important role in evolution of Mars. Also the plains and old cratered terrains are interpreted to be volcanic. The total volume of volcanic material produced through martian history was estimated [3] to be $68.80 \times 10^6 km^3$. This is rather conservative value comparing to other authors and the estimates of total volume of magmatic products are comparable to the size of the martian crust.

The amount of water that was released varies[4,5]. Clifford [5] estimates that the northern hemisphere ocean was 10^2–10^3 m deep and the amount of water was 6.5×10^7 km^3. Model of martian hydrosphere [5] suggests that the amount of outgassed water exceeds volume of cryosphere calling thus for subpermafrost ground water system.

It is highly likely that substantial part of volcanic activity has taken place in form of pyroclastic eruptions. In terrestrial environment pyroclastic deposits are associated with the presence of water in magma and with "bubble bursting" when pyroclastic deposits are formed. The similarity of volatile element composition in martian atmosphere and SNC meteorites suggests and numerous authors have argued that loss of the volatiles occurred in the early history of Mars.

The history of early outgassing is apparently similar for the Earth and Mars though later evolution has taken different paths. The idea of origin of the atmosphere and hydrosphere [6] via analogy with the recent volcanic gasses (H_2O, CO_2, H_2S) suggests that Earth's O-bearing atmosphere is secondary and its chemistry results from the evolution of life. In order to compensate for the faint Sun in the early history of Earth as well as Mars greenhouse gasses CO_2, methane, ammonia served as temperature regulators. And warmer and wetter climate has been proposed for Mars.

The presence of water, high CO_2 in the atmosphere and warm climate lead to intense weathering of silicates, consumption of CO_2 and formation of protoocean which is "soda ocean" rather than modern "halite ocean"[6].

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O—>$$
$$Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$
(albite) (kaolinite)
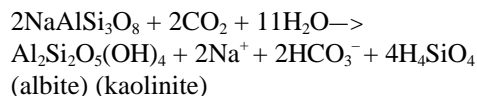
Ocean formed through such weathering has alkaline character because of high solubility of Na^+ and K^+ carbonates whereas Ca^{++} precipitates in $CaCO_3$. Soda ocean (on the Earth) is in equilibrium with the atmosphere that lacks atmospheric molecular O and is compositionally similar to alkaline lakes in volcanic areas (Turkey, East African rift zone) and soda lakes in terrestrial non-drained environments (Basin and Range province).

The reaction of soda ocean and infalling pyroclastic rocks of basaltic composition results in the formation of zeolites[7,8].

$$NaAlSi_3O_8 + H_2O —> NaAlSi_2O_6.H_2O + SiO_2$$
albite + water zeolite (analcime) + quartz
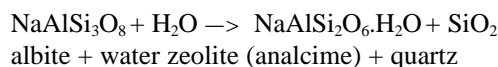
Because of their properties zeolites could influence the behavior of volatiles in early Mars and early Earth. Rather sudden decrease of volatiles contents in the Mars atmosphere may have been caused by the intense volcanism and formation of zeolites that have a remarkable adsorption features.
A natural zeolite is a framework alumo-silicate whose structure contains channels filled with water and exchangeable cations. Ion exchange is possible at low temperature (100°C at the most) and water is lost usually in steps in a large range of temperatures (150° to 400°C) mostly at about 250°C and reversibly readsorbed at room temperature. The general formula for natural zeolites is

$$(Li,Na,K)_a(Mg,Ca,Sr,Ba)_d[Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}]\ mH_2O$$
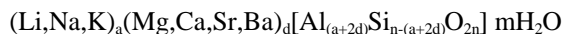
where the part in square brackets represents the framework atoms and the part outside the square brackets represents the extra framework atoms, cations plus water molecules and allows enormous mineralogical variability within the zeolite family and also within a single zeolitic species [7]. In place of water the gases can be adsorbed, up to 10 wt% in case of CO_2 or O_2. This feature is employed during the separation of gases in landfills. Thus zeolites could be responsible for the vigorous exchange (isotopic exchange) between the crust and atmosphere.

Scenario for Mars (and idea of zeolite presence in martian surface is not new [9]) involves intense weathering, formation of alkaline "soda ocean", very intense

basaltic volcanism followed by formation of zeolites and the absence of plate tectonics that allows among other processes the circulation of water between lithosphere and hydrosphere reservoirs. Jakosky and Jones [1] have noted that "the isotopic evidence requires substantial exchange of volatiles between the atmosphere and the crust of Mars. This exchange must have postdated the early periods that included the hydrodynamic outflow epochs as well as the earliest epochs recorded in the geologic history". These processes have taken place during occasional warmer and wetter environments, probably in soda ocean in the presence of zeolites. In the search for the non-atmospheric reservoir of volatiles. Zeolites are excellent candidates. In the search for extremophile (martian) organism zeolites should be looked closely since catalytic features in direct toward and their ability to act as molecular sieves and exchange cations with the change of temperature conditions (e.g., diurnal adsorption of water and gasses).

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POLYCYCLIC AROMATIC HYDROCARBONS ARE EVERYWHERE IN ALLAN HILLS 84001.

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Introduction: Polycyclic aromatic hydrocarbons (PAHs) observed on fracture surfaces of the Martian meteorite ALH 84001 were suggested as a major evidence for possible relic biogenic activity on our neighboring planet [1]. In general, the origin of PAHs is not restricted to biological processes, but the proposed spatial association of PAHs with carbonates that in turn contain internal structures resembling terrestrial microfossils was taken as evidence for a genetic link between both observations [1]. This, however, would contradict the results of an earlier study of ALH 84001 that demonstrated (i) that the PAH enrichments do not *always* correlate with carbonates and (ii) that some carbonates in this meteorite do not contain PAHs [2]. With the technique used in both these studies, microprobe two-step laser mass spectrometry ($\mu L^2 MS$), an unambiguous determination of a spatial association is limited by the lateral resolution of the instrument, about 50 µm, a size that is comparable with the typical dimension of the carbonates.

We used time-of-flight secondary ion mass spectrometry (TOF-SIMS) with a lateral resolution of about 0.2 µm to investigate the possible relationship between PAHs and carbonates. Here we report on our research of the spatial distribution of PAHs in two more sections of ALH84001 that continues our previous study of another section [3].

Results: Time-of-flight secondary ion mass spectrometry analyses of all three investigated thin sections revealed PAHs. The secondary ion mass spectra have identical characteristics. The preferential occurrence of low-mass PAH ions and the presence of positively charged radical ions are both attributed to fragmentation by the primary ion bombardment [3]. The previously found general trend of a lower content of PAHs in carbonates than in orthopyroxene or feldspatic glass is corroborated by the present follow-up analyses. Moreover, no pronounced PAH enrichment was detected with TOF-SIMS in any of the investigated carbonates.

Surface contamination is a major concern in TOF-SIMS analysis since the information depth in a typical measurement is of the order of a few atomic monolayers. The three investigated thin sections stem from three different chips of ALH84001 and were prepared at different times in two different laboratories. This should minimize the probability of a common contamination with external PAHs during processing. A section of Chassigny [4] that was treated exactly like one of our ALH 84001 sections and measured directly before and after ALH 84001 contained no PAHs. In an attempt to further investigate the (possible) contamination problem we employed various sputtering techniques: (i) extensive sputtering and analyzing with Ga^+ ions alone, (ii) simultaneous sputtering with Ar^+ and analyzing with Ga^+, (iii) analyzing with Ga^+ after sputtering with Ar^+. The complex results open a variety of interpretations. In one case we observed a slight increase of the PAH signals during sputtering. Another section first had a rather uniform distribution of PAHs on the very surface, and, after extensive sputtering, the PAH signals decreased but did not vanish. Their intensities vary between different minerals and again reveal the previously observed "anti-correlation" of PAHs and carbonates. Their uniform distribution before sputtering might indeed be the result of polishing, i.e., of redistribution of PAHs that are indigenous to the meteorite.

Discussion: The origin of the omnipresent PAHs in ALH 84001 cannot be deduced as yet from our TOF-SIMS experiments. However, we exclude a spatial association of PAHs with carbonates and consequently also with nanostructures supposedly present within carbonates. Therefore, a genetic link between the proposed nanofossils and PAHs appears to be improbable. Both observations are to be understood independently. Since the biogenic interpretation of the phenomena observed in ALH 84001 relies mainly on their collective explanation [1] it seems to be highly questionable.

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A "UNIQUE" DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN ALLAN HILLS 84001, OR A SELECTIVE ATTACK IN METEORITES FROM MARS?

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Introduction: McKay et al. [1] detected polycyclic aromatic hydrocarbons (PAHs) in the Antarctic meteorite ALH84001 and claimed that they were distinct from those in terrestrial samples and carbonaceous chondrites (CCs) due to their lack of alkylation and low mass components. When considered with other results from this meteorite they concluded that the PAH were fossilized products of martian life. Subsequently Becker et al. [2] detected this "unique" distribution of PAH in another Antarctic martian meteorite (EETA79001), Antarctic CCs and the Antarctic ice itself. To investigate the causes of these PAH distributions we analysed the organic matter (OM) in 10 CM meteorites which represented both non-Antarctic falls and Antarctic finds.

Methods: Powdered unextracted meteorites were subjected to pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) as in [3].

Fig. 1

Results: Comparing the Murray results from Fig. 1. and ref. [4] reveals that Py-GCMS and the L^{2}MS procedure used for ALH84001 give different responses for the same samples. Unlike L^{2}MS, Py-GCMS analyses the total OM present, i.e. small amounts of evaporated free compounds and larger amounts of degraded macromolecular material. Hence direct comparisons with ALH84001 are difficult. However, Fig. 1. reveals significant differences between the OM of Antarctic and non-Antarctic CCs. The released products from Antarctic CCs are less structurally diverse and benzene is significantly enhanced relative to toluene.
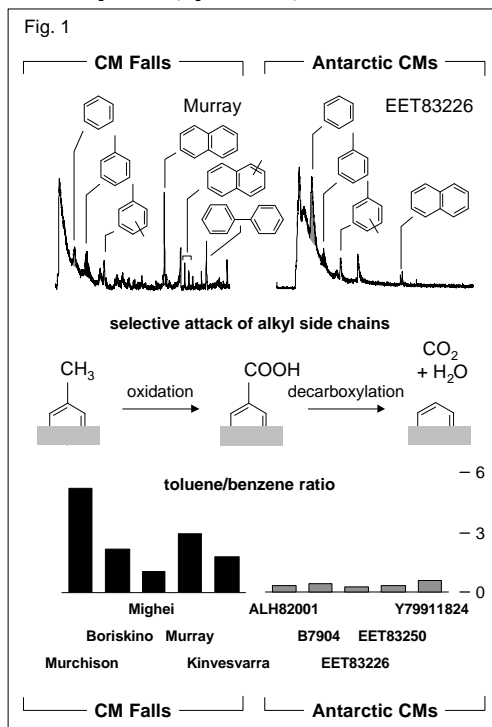
Discussion:

Antarctic PAH. OM in Antarctic meteorites appears substantially altered from its fall state. The effects of Antarctic weathering on meteoritic OM are poorly understood but the results of weathering on terrestrial OM are known [5]. One common feature is the preferential oxidation of aliphatic OM present as alkyl side chains. This process would explain the differences in toluene/benzene ratios from the non-Antarctic and Antarctic CMs (Fig. 1). Consequently, Antarctic PAH from any source may exhibit less alkylation than when unweathered. Therefore the unalkylated PAH distribution in ALH84001 appears more of a characteristic of the Antarctic environment than fossil Martian life. It is for this reason that similar distributions are found in other examples of Antarctic OM [2].

Implications. The effects of weathering on Antarctic meteoritic OM indicate that if its origins are to be investigated, methods must be applied to compensate for the loss of structural information by oxidation. ALH84001 contains 20 % indigenous C as an insoluble, possibly organic phase [6]. Therefore small-scale hydrous pyrolysis of this component followed by isotopic measurements of the products [7] would be appropriate.

Conclusions: During its time in Antarctica, meteoritic OM is weathered. Py-GCMS indicates that PAH alkyl side chains are selectively oxidized in free and macromolecular OM. Future interpretations based on PAH distributions in meteorites should take this process into account.

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TERRESTRIAL CONTAMINATION OF AN ANTARCTIC CHONDRITE. A. Steele[1], D. T. Goddard[2], J. K. W. Toporski[3], D. Stapleton[3], D. D. Wynn-Williams[4], and D. McKay[1], [1]Mail Code SN2. NASA Johnson Space Center, Houston TX 77058, USA, [2]Research and Technology, BNFL, Springfield works, Preston PR4 0XJ, UK, [3]Department of Geology, University of Portsmouth, Portsmouth PO1 2DT, UK, [4]British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK.

The question of the existence of terrestrial organic contaminants in the Martian meteorite ALH 84001 has raised doubts over the pristine nature of Antarctic meteorites. In recent papers Bada and Jull (1997) show the presence of terrestrial organic contamination and conclude that the source of these compounds was the Antarctic ice (1,2). In the last decade there has been a revolution in our understanding of the organisms which colonise extreme environments, including Antarctica. A large number of organisms including bacterial, fungal and lichen species have been shown to inhabit Antarctic lakes ice and rocks eg. Cryptoendolithic communities [3,4].

In an attempt to elucidate whether terrestrial organisms could be involved in the contamination of Antarctic meteorites we examined two carbonaceous chondrites (ALHA 81024,26 C/B; ALHA 77176,11 B) and two ordinary chondrites (ALHA 81251,17 B/C; ALHA 76004,21 A/A). The meteorites were mounted onto stubs using carbon tape and sputter coated with Au/Pd for 30 s before imaging by scanning electron microscopy (SEM). Several rock samples from the Timber Peak region of Antarctica which are known to contain cryptoendolithic communities were also imaged under the same conditions as the meteorites.

Our preliminary investigations show the presence of a hyphae producing organism on ALHA 76004 (Fig. 1a). This organism resembles the fungal species shown to be present in the Timber Peaks cryptoendolithic samples (Fig. 1b). This clearly demonstrates that these meteorites can harbor the resident Antarctic microbiota. Mautener et al. (1997) have already shown that it is possible to produce thriving colonies of terrestrial bacteria from the nutrients contained in an ordinary chondrite [5]. To our knowledge this is the first recorded case of a terrestrial organism colonising and contaminating an Antarctic blue ice field meteorite. However, it is unlikely to be the last. Since the controversy over ALH 84001 the issue of Antarctic contamination has gathered impetus and more serious attempts are being made to define the depth of the problem. Our research has shown that out of 4 meteorites examined, one definitely contained evidence of colonisation by a terrestrial organism. Any analysis of the organic molecular species in ALHA 76004 could be significantly influenced by the presence of this organism, although the sample was taken from only 2–3mm from below the fusion crust. Certain questions arise from this research, how many other meteorites have been contaminated and to what extent? What is the rate and depth of penetration of the contaminant organisms into the meteorite? And how can we detect and nullify the effects of terrestrial contamination during analysis?
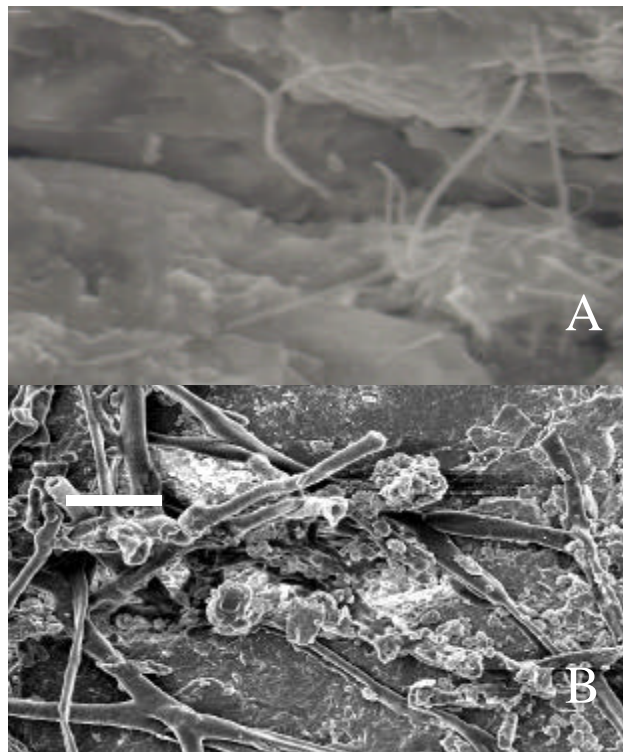
Fig. 1. **(a)** Image of Fungal like organism found on ALHA 76004 (×7500). **(b)** Image of a similar organism from the Timber peaks cryptoendolithic community (×20000). Scale bar = 1μm

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HYDROTHERMAL MODIFICATION OF SULFIDES IN NAKHLA, LAFAYETTE, AND CHASSIGNY.

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Ion microprobe sulfur isotope analyses of sulfides in the putative martian meteorites Nakhla and Chassigny point towards complex formation processes [1]. The nakhlites (Nakhla, Lafayette, and Governador Valadares) and Chassigny have similar cosmic ray exposure ages [2], suggesting that they may be derived from the same impact event, and are thus geographically related. Preliminary results for sulfur isotopic analyses of pyrite/marcasite in Lafayette, pyrrhotite/chalcopyrite in Nakhla, and pyrite in Chassigny suggest that sulfides in these meteorites may be closely related and have been modified by hydrothermal fluids with light sulfur isotopic values.

Results: <u>Chassigny:</u> Although pyrite is the only sulfide phase we have identified in our sample thus far, pentlandite and troilite were reported as minor sulfides in Chassigny by [3]. The pyrite is intergrown with oxides (probably chromite), and appears to be a primary subsolidus texture. $\delta^{34}S_{CDT}$ values of pyrite in Chassigny range from -1.5 to -4.3‰ with a mean of -2.9‰. <u>Nakhla:</u> Pyrrhotite is the main sulfide phase with $\delta^{34}S_{CDT}$ ranging from -1.7 to +4.9‰ and a mean of +1.5‰. Minor chalcopyrite can be associated with pyrrhotite. The sulfides and oxides are found interstitially in association with the mesostasis and are best described as late-stage magmatic features. One large pyrrhotite grain has a veinlet of chalcopyrite cutting it, clearly indicating a later event. $\delta^{34}S_{CDT}$ values of another chalcopyrite/pyrrhotite grain (-2.0, -2.1‰/ +0.4, -0.1, +1.0‰, respectively; 1σ <0.8‰) are reversed, indicating isotopic disequilibrium [4]. <u>Lafayette:</u> Our observations of opaque mineralogy are similar to [5], with the exception that in our section marcasite (as opposed to pyrite) is the most common sulfide. In one instance, marcasite is found replacing pyrite. Marcasite always has textures indicative of replacement; in one instance it is observed replacing pyrite. There are two populations of oxides in Lafayette. Many of the oxides and sulfides occur interstitially associated with mesostasis and iddingsite, similar to Nakhla. Another set of oxides occurs in the silicates, and is much less altered than those associated with mesostasis. The oxides in Lafayette have undergone more extensive alteration (evidenced by abundant "exsolution" lamellae) than in Nakhla. The range of $\delta^{34}S_{CDT}$ of pyrite/marcasite as determined by ion microprobe in Lafayette is -5.1 to +0.1‰ with a mean of -3.5‰ (5 of 6 analyses were -3.2 to -5.1‰).

Discussion: The isotopically light marcasite and pyrite in Lafayette and Chassigny, as well as the isotopically light chalcopyrite in Nakhla, are significantly removed from the postulated Mars mantle $\delta^{34}S_{CDT}$ Å 0‰ [6]. Mineralogy, light $\delta^{34}S$ values, and isotopic disequilibrium between sulfide phases are consistent with alteration by late-stage, oxidizing hydrothermal fluids. Differences in sulfide mineralogy between Nakhla and Lafayette, possibly from the same igneous unit [8], may be related to different subsolidus thermal histories [8]; marcasite and pyrite may have replaced pyrrhotite in Lafayette.

Incorporation of sulfur from country rock is common in terrestrial magmatic intrusions [7]. A possible scenario to explain the light sulfur isotopic values of disulfides in Nakhla and Lafayette is by reaction of primary pyrrhotite with isotopically light sulfur-bearing fluids. Pyrite in Chassigny may have been precipitated directly from these fluids. Future work is planned on Lafayette and Governador Valadares.

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OXYGEN ISOTOPES IN WATER FROM MARTIAN METEORITES. L. Baker, I. A. Franchi, I. P. Wright, and C. T. Pillinger, Planetary Sciences Research Institute, The Open University, Milton Keynes, MK7 6AA, UK. (L.Baker@open.ac.uk).

Introduction: Those meteorites of supposed martian origin which have been analysed thus far, have water contents of between 0.04 and 0.4 wt % [1,2]. A complete understanding of the nature and origins of this "water" is of paramount importance. One potentially useful way forward is through measurement of stable isotopic compositions (δD, $\delta^{17}O$ and $\delta^{18}O$). Herein we apply our new water pyrolysis technique [3] to the problem in order to obtain oxygen three isotope information.

Technique: We used ~50 mg samples of two different martian meteorites, Nakhla and ALH84001. These were pyrolised over a range of temperatures from 50–1000°C in 100° steps of about 20 minutes duration. Volatiles evolved were swept directly onto a fluorinating agent (CoF_3), where water was converted to O gas. The reaction by-product, HF, together with any other contaminants were removed by chemical and cryogenic traps. A GC column further purified the sample before passage to the mass spectrometer.

Results: The two samples analysed herein are shown in Fig. 1. Whilst Nakhla has been analyzed previously in a different laboratory [1] this is the first time that the O isotopic composition of water in ALH84001 has been determined. Nakhla shows a simple water release curve with a peak at lower temperatures of ~200-300°C before tailing off at higher temperatures. The $\delta^{18}O$ values show a similar but more pronounced trend than that previously observed by [1] with a distinct low temperature component and another at higher temperatures. The better resolution of the $\delta^{18}O$ signal may be the result of our rigorous efforts to reduce memory effects. The profile of ALH84001 shows that more water is retained to higher temperatures, the yield not tailing off until after the 500°C temperature step. The release up to 500°C shows two peaks each of which appears to have a distinct $\delta^{18}O$ signature. In common with Nakhla, $\delta^{18}O$ reaches a peak value at about 600°C before falling again at higher temperatures. $\Delta^{17}O$ values (not shown for reasons of clarity) from Nakhla are very similar to those published previously [1]. Equivalent data from ALH84001 show a similar overall pattern to Nakhla demonstrating the presence of isotopically distinctive water components.

Discussion: In a previous study of D/H ratios from eight martian meteorites [2] water released up to about 300°C had δD values compatible with water of terrestrial origin. That released at higher temperatures had δD values between +100 and +2000‰, suggestive of a martian origin for this component as the atmospheric δD of Mars is about +4,000‰ [4]. For the samples analyzed herein, water released at low temperatures is dominated by terrestrial contamination. In the case of Nakhla this appears to be represented by a single peak at 200°C, perhaps representing a single period of terrestrial alteration. In contrast the release from ALH84001 shows evidence of two distinct components at low temperatures, one at 200°C and one at 400°C. This is suggestive of a more complex terrestrial alteration history, in keeping with its relatively longer terrestrial age. Exposure to isotopically light Antarctic ice may also explain the relatively lower $\delta^{18}O$ signal from the high temperature steps which peak at +2‰ as opposed to +6‰ for Nakhla.
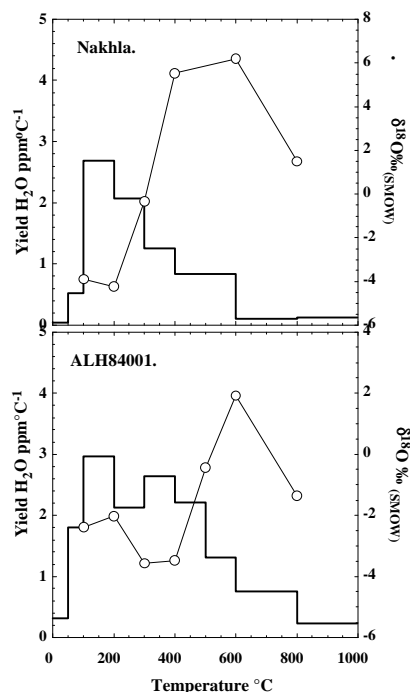
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OXYGEN ISOTOPIC COMPOSITION OF MARTIAN CARBONATE AND HIGH-RESOLUTION SECONDARY ION MASS SPECTROMETER IMAGING OF THE ALTERATION ASSEMBLAGE IN LAFAYETTE METEORITE.

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Introduction: Carbonate from SNC meteorites offer us insight into a variety of processes on and/or beneath the surface of Mars. In Lafayette, carbonate occurs in unusually intimate association with hydrous phases when compared with other carbonate-bearing SNCs [1]. We have measured the $^{18}O/^{16}O$ ratio of carbonate in the alteration veins of Lafayette using the magnetic sector ion microprobe. In addition, we obtained isotope images of major and minor element cations in veinlets with the Focused Ion Beam (FIB) quadrupole SIMS. The size of the FIB probe used in this study (~ 0.03 micrometers) provides an opportunity for high spatial resolution chemical imaging which is ideal for examining features in the fine-grained alteration assemblage.

Carbonate oxygen isotope chemistry: While data presented here are the first reported *in situ* oxygen isotope analyses of Lafayette carbonate, several studies have been performed on released CO_2 by vacuum pyrolysis and acid etching [2-4].

Summary of previous bulk CO_2 measurements. The spread in values of $\delta^{18}O_{SMOW}$ for released CO_2 is reasonably large and ranges from 22-33 ‰ (high to low T pyrolysis, respectively [2]), with a single measurement of 10.5 ‰ (144 hr etch [4]) that falls below this range. The latter measurement clearly includes a terrestrial component indicated by its carbon isotopic composition [4]. Both pyrolysis studies [2,3] emphasize the possibility of equilibration with oxygen from silicates and released water during extraction. Despite this uncertainty the authors concluded that oxygen from released CO_2 is sufficiently heavy relative to the whole-rock that it represents a phase out of equilibrium with magmatic silicates. They further conclude that this observation is consistent with carbonate deposition at low temperature.

Ion microprobe results. Carbonate within four olivine-hosted veinlets (each from a different host crystal) were measured for their oxygen isotopic composition with a Cameca 4f ion microprobe. The major element composition of the carbonate differs little among the veinlets and typically has a composition $(Fe_{65}Mn_8Ca_{27}Mg_{0.2})CO_3$. Corrections for the major element composition of Lafayette siderite relative to

isotopic standards are identical to the methods used by Eiler et al. [5].

The $\delta^{18}O_{SMOW}$ values from the 4 veinlets are as follows: 30.8 ± 0.9 ‰, : 30.7± 1.1 ‰, 34.8 ± 0.8 ‰, and 36.2 ± 0.8 ‰ (uncertainties expressed as 1 σ internal). Regions of siderite in Lafayette are rarely greater than 25 micrometers in width. Postmortem scanning electron images of the ~20 micrometer sputter pits were collected. These images revealed a minor volume of silicate incorporated into the two analyses which yielded results of ~30 per mil, while the veinlets with values of $\delta^{18}O$ of 35-36 per mil (Figures A,B) appear to be pure carbonate. These compositions are among the heaviest oxygen reported for martian carbonate and are indistinguishable, within analytical uncertainty, from the results of Saxton et al. [6] for siderite from Nakhla. The high $\delta^{18}O$ of Lafayette siderite and the striking similarity of the isotopic composition to Nakhla carbonate suggest a common origin, perhaps by precipitation from a low temperature aqueous fluid as is required by closely associated iddingsite in Lafayette. Without knowledge of the isotopic composition of martian crustal fluids we cannot use our results to quantify the temperature of carbonate formation, but based on previous estimates of plausible compositions for such fluids our results are consistent with the low temperatures (< 70°C) estimated for alteration fluids from previous studies of Lafayette [7,8].

Secondary ion imaging of alteration products: The Focused Ion Beam is a relatively new micro-machining and -analytical tool and has to date been best exploited by those in the semiconductor industry. We used a FEI FIB200 that employs a liquid Ga ion source. Primary ions were accelerated to 30kV while secondary ions were collected in (+) mode with a quadrupole mass spectrometer. A probe current of ~5 pA was selected to obtain high resolution images of ^{23}Na, ^{24}Mg, ^{27}Al, ^{28}Si, ^{39}K, ^{40}Ca, ^{55}Mn, and ^{56}Fe in the carbonate-hydrous silicate-transition metal oxide alteration assemblage, often referred to as "iddingsite" (Figures C-G). ^{39}K images reveal intricate banding parallel to the long axis of the veinlet in the central-most region that is filled with ultra fine-grained phyllosilicate, as well as enrichment in coarser-grained

clays oriented perpendicular to banding (Figures D,E). The K distribution between these two phases in iddingsite may help to explain the wide range of formation ages (100-655 Ma) determined by ^{40}Ar-^{39}Ar [9] and K-Ar [10] as Ar retentivity is probably poorer in the finer-grained material. Furthermore, ^{23}Na imaging indicates a surprisingly high ion yield from regions that are virtually pure siderite (EPMA totals ~ 99 wt%). The source of the Na is likely from a nanometer-scale inclusions of salts noted in a previous studies of Nakhlite alteration [7,11], and provides further evidence for the saline nature of the Lafayette alteration fluid.

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Fig. 1. **(a)** Backscattered electron (BSE) image of an olivine-hosted alteration veinlets. Termination of the veinlet at the pyroxene grain boundary suggests that alteration is essentially restricted to olivine. Darker material within the veinlet represents ultra fine-grained phyllosilicate. ^{18}O/^{16}O measurement site indicated by arrow. **(b)** BSE image of rare veinlet filled nearly completely by carbonate. **(c)** Ion-induced secondary electron (SE) image. Because of differential sputtering of alteration minerals the SE signal carries compositional information at greater resolution than high energy BSEs. Greyscale banding parallel to the long axis of the veinlet represents "iddingsite." The bracket encloses layers of smectite (dark grey oriented crystals perpendicular to vein walls), transition-metal oxides (light grey), and ultra fine-grained phyllosilicate (darkest grey, veinlet center). **(d)** Fine-scale K banding in the alteration veinlet above (view is rotated and tilted relative to SE image in C. **(e)** Higher magnification ^{39}K image of central portion of D. **(f)** Ion image showing low concentration but uniform distribution of ^{23}Na within siderite. **(g)** ^{40}Ca image provides a high contrast display of the carbonate along the margins of the veinlet with apparent substitution of minor Ca in Fe-Mn oxides.
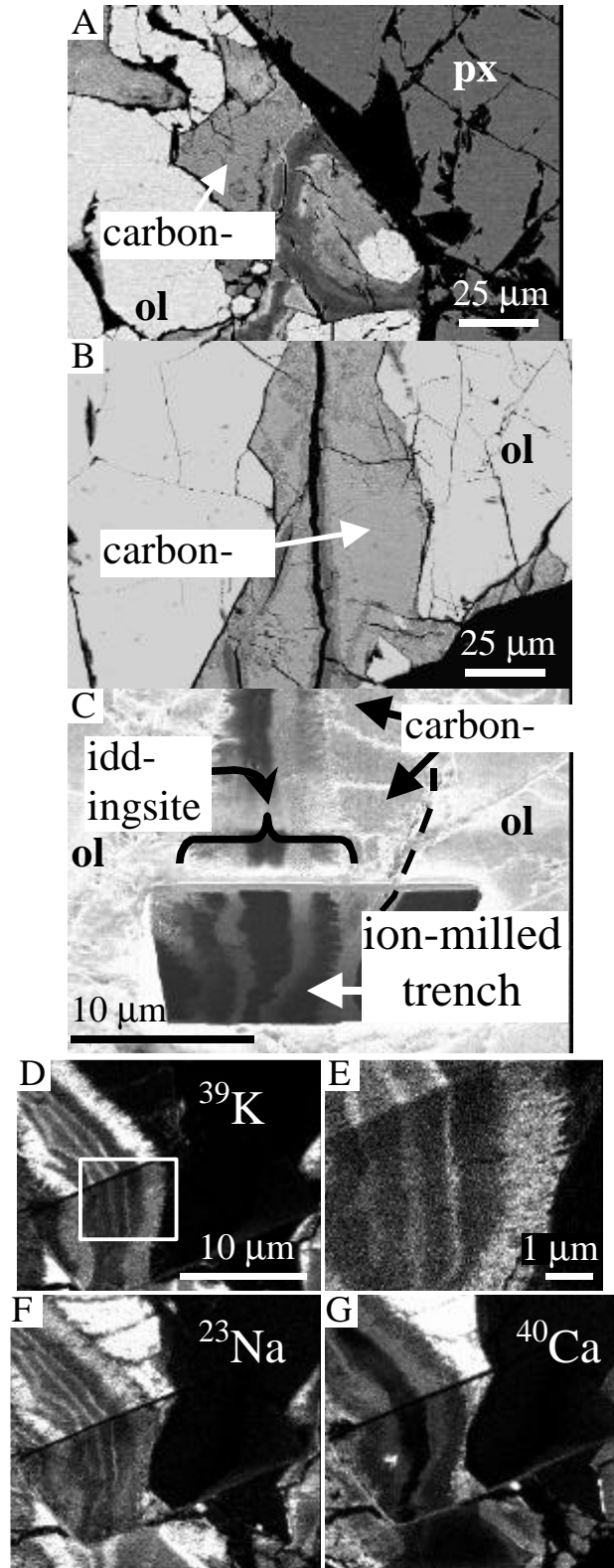
OXYGEN ISOTOPIC COMPOSITION OF NAKHLA SIDERITE: IMPLICATIONS FOR MARTIAN VOLATILES.

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We have previously [1] reported O isotopic measurements of two grains of Mn-rich siderite in Nakhla. The four measurements were identical within error, yielding mean $\delta^{18}O = 34 \pm 1$‰ SMOW. This is the heaviest carbonate yet reported from a martian meteorite. We now explore the implications of these data for martian volatiles.

Various authors have considered the isotopic composition of martian volatiles. Clayton and Mayeda [2] considered production of a hydrosphere and atmosphere by high-temperature outgassing of CO_2 and H_2O, followed by cooling to low temperature. This process can also be considered on a local scale [e.g., 3,4]. An alternative view taken by Hutchins and Jakosky [5] suggests the hydrosphere/atmosphere was enriched in heavy isotopes; this would render models that involved high-temperature fluid-silicate equilibrium inappropriate. It is also possible that, by the time the Nakhla carbonate formed, the $\delta^{18}O$ of the hydrosphere could have been reduced through fixation of CO_2 as carbonate; assuming fixation as $CaCO_3$ at 0°C we estimate $\delta^{18}O$ may be reduced by ~4–6‰ by this process.

In Fig. 1 we relate the siderite $\delta^{18}O$ and formation temperature to these potential martian H_2O/CO_2 reservoirs. In the lefthand panel we show $\delta^{18}O$ of H_2O/CO_2 produced by initial outgassing (after [2]); X is the mole fraction of O as water in the degassed reservoir. Clayton and Mayeda suggested X ~ 0.8 since it could account for their measurements of the carbonate in EET 79001. In the righthand panel, we postulate a hydrosphere/atmosphere at 0°C from which is taken a sample of fluid having mole fraction X oxygen as water. This sample of fluid is then heated to temperature T, at which siderite forms in equilibrium with it. No fluid-silicate isotope exchange takes place. Figure 1 shows $\delta^{18}O$ of the H_2O and CO_2 of the hydrosphere/atmosphere required to obtain siderite having $\delta^{18}O = 34$‰. Bridges and Grady [6] have suggested that the Nakhla siderite formed from a melt, derived from the melting of sediment. On this view, the siderite $\delta^{18}O$ — and the present discussion — refer to the precursor sedimentary siderite.

Comparing the two panels of Fig. 1, we see that at low temperatures, $\delta^{18}O$ of the H_2O and CO_2 lie within the range of values that may be produced by initial outgassing, provided X is sufficiently high. Therefore our data do not require a hydrosphere-

atmosphere highly enriched in ^{18}O, which might have been expected by analogy with atmospheric H, C, and N. For T > 60°C, if the siderite formed from a water-rich fluid (X → 1) the inferred values of $\delta^{18}O$ of the H_2O and CO_2 are too high to be consistent with fluids produced by initial outgassing and subsequently unmodified.

The siderite $\delta^{18}O$ also places a lower limit on $\delta^{18}O$ of present-day CO_2 of ~40‰ (or ~36‰ if the siderite equilibrated with water (brine) at –20°C). After making a simple allowance for low-temperature H_2O_{vapor}-CO_2 fractionation, this is consistent with terrestrial IR spectroscopy [7].
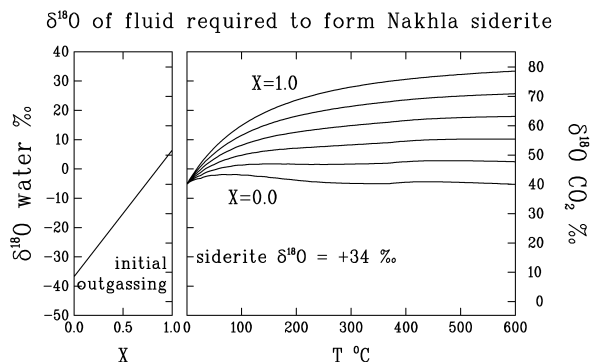
Fig. 1.

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TRACES OF MARTIAN SEDIMENT IN NAKHLA AND OTHER SNC METEORITES.

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Introduction: We report some results of a search in Nakhla, Lafayette and EETA 79001 for mineralogical and trace element evidence of trapped martian sediment. The origin of these meteorites' parent rocks on or near the martian surface means it is likely that traces of sediments were incorporated into them. Salt pan deposits formed by evaporative concentration of ground or standing water are thought to exist on Mars [1]. Such evaporites would contain halite, anhydrite and carbonate. These could be incorporated with igneous rocks by 3 mechanisms: melting and incomplete mixing with crystallising lava [2]; hydrothermal remobilisation [3] and entrainment during shock melting [4]. The addition of sedimentary components, which had been in exchange with the martian atmosphere, can help explain isotope signatures such as the high $\delta^{13}C$ values in carbonate from SNCs [5]. The first mechanism is seen in Nakhla, the second is most clearly displayed in nakhlites [3], the third in EETA79001 [4].

Nakhla: A halite-siderite-anhydrite assemblage has textures which suggest it crystallised at 800-1000°C from an ionic melt [2]. It is associated with interstitial silicate rather than being spread throughout the rock in cracks or voids. In some areas halite has crystallised around grains of plagioclase and silica [2] whereas in others, the salt melt has forced open cracks leading from interstitial silicate into the margins of surrounding olivine and augite grains. Neither texture is consistent with deposition from low temperature hydrous fluids such as those associated with the clay veins. Siderite can be stabilised at high temperatures by Na and Cl. The trapped salt melt component contains 97% halite, 2% siderite, 1% anhydrite and traces of chlorapatite. Contrasting trace element abundances between siderite in Nakhla and terrestrial hydrothermal siderite (Figure) are further evidence that the former crystallised at high temperature. Variation in REE abundances between Nakhla siderite grains is due to extraction of REE-free halite from ionic melt fractions.

Clay in Nakhla and Lafayette: EDS analyses of smectite/illite veins show they contain ≤ 3.7 wt% Cl in Nakhla and ≤ 0.2 wt% in Lafayette. No halite has been found associated with Nakhla clay in this or other studies [3]. A late generation of sulphate and calcite is associated with it [3]. Halite has not yet been found in Lafayette. This together with relatively low Cl abundances in the clay suggest that the La-fayette parent rock originated in a less halite-rich area of the martian surface than Nakhla.
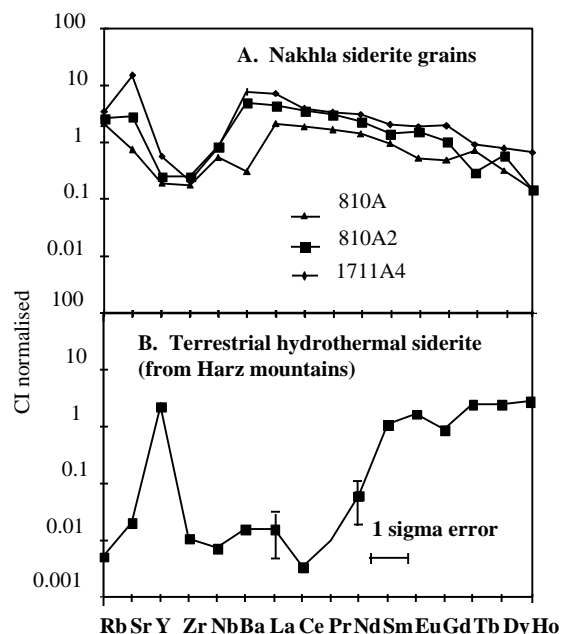
Fig. 1. Trace element abundances of Nakhla and hydrothermal siderites determined by Cameca IMS3f ion-probe with -^{16}O beam at 15kV (Edinburgh University, NERC supported facility).

Elephant Moraine 79001: Some sulphates and Ca-carbonate were derived by assimiliation into the parent during shock induced melting at ≥ 1100°C [4]. We are studying new sections in an attempt to provide information on the relationship between martian sediments and this assemblage.

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BRINE EVAPORATION: AN ALTERNATIVE MODEL FOR THE FORMATION OF CARBONATES IN ALH84001.

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Globules and lacy networks of Mg-Fe-Ca carbonates occur within impact-produced fracture zones in the ALH84001 martian meteorite. Because these carbonates are associated with the hydrocarbons, putative biogenic minerals, and microfossils that collectively have been cited as evidence for ancient martian life [1], it is critically important to understand their formation. Previous hypotheses invoke either alteration of the rock by hydrothermal fluids at relatively low temperatures [2] or formation from a CO_2-rich vapor at high temperatures [3].

In the spirit of multiple working hypotheses, we explore an alternative mechanism, that of direct precipitation from an evaporating brine. The evaporative saline waters may have ponded in a restricted drainage basin, such as an impact crater, and infiltrated fractures in the crater floor. High-albedo features in some martian craters have been interpreted as playas formed by evaporation [4], martian soil analyses indicate high salt concentrations [5], and brines have been implicated in the alteration of martian meteorites [6]. Evidence for evaporation on Mars must be balanced against the likelihood that surface water might freeze rapidly, but high solute concentrations would depress the freezing point of brines.

The compositions and zoning trends of the carbonates in ALH84001 [3] appear to be broadly consistent with this model, and associated sulfides and silica and lack of phyllosilicates are characteristic of some terrestrial evaporites. The isotopically heavy C of the carbonates [6] is easily reconciled with a requirement for previous cycling of C through the martian atmosphere, and evaporation provides an alternative explanation for the observed O isotopic fractionations [7]. Although minor Fe-sulfate was tentatively identified in ALH84001 [8], the lack of abundant sulfate and other salts seems inconsistent with an evaporite deposit. However, terrestrial alkaline lakes are commonly stratified so that the precipitation sequence is developed as geographically concentric zones. Near the edges of evaporating lakes, carbonate zones showing progressive Mg enrichment can form, without associated sulfates and other salts. Occlusion of pore spaces in the underlying rocks with carbonate before the onset of sulfate precipitation may also explain explain the absence or salts.

The formation of carbonates by this mechanism implies that they are relatively old, and that their radiometric ages may be indeterminate unless an isochron involving evaporites alone can be measured. A role for microbial organisms in the precipitation of the carbonates [1] seems possible in this environment but unnecessary, as the evidence for life can better be explained by abiotic processes. Evaporites may provide unambiguous evidence for water persisting at one location on Mars for a significant time. Consequently, formerly flooded craters in the ancient highlands may become sites of choice for exploration by future Mars landers.

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PETROLOGIC EVIDENCE FOR LOW-TEMPERATURE, POSSIBLE FLOOD-EVAPORITIC ORIGIN OF CARBONATES IN THE ALH84001 METEORITE.

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High-temperature models for origin of the carbonates in martian meteorite ALH84001 are implausible. The impact metasomatism (vapor-deposition) model [1], invoking reaction between fluid CO_2 and the host orthopyroxenite, implies a higher than observed proportion of residual void space. It also requires conversion of olivine into orthopyroxene, yet olivine in ALH84001 shows no depletion in carbonate-rich areas; or else conversion of orthopyroxene into silica, which should have yielded a higher silica/carbonate ratio. Likely CO_2-vapor sources would tend to also add sulfates. Complex variants, assuming a large volume of fluid coursed through ALH84001, might alleviate the void space and silica deficit problems, but take on unattractive features of the hydrothermal model, discussed below. The impact melt model [2] implies that the fracture-linked carbonates, as products of melt injection, should appear as continuous planar veins, but in many areas they do not. The premise that rapid crystallization of impact melt determined the final distribution of the feldspathic matter is contradicted by the typically equant-granular shape of zones of feldspathic glass framed by lacy carbonates. Both vapor deposition and impact melting seem inconsistent with the zoned poikilotopic texture of many large carbonates.
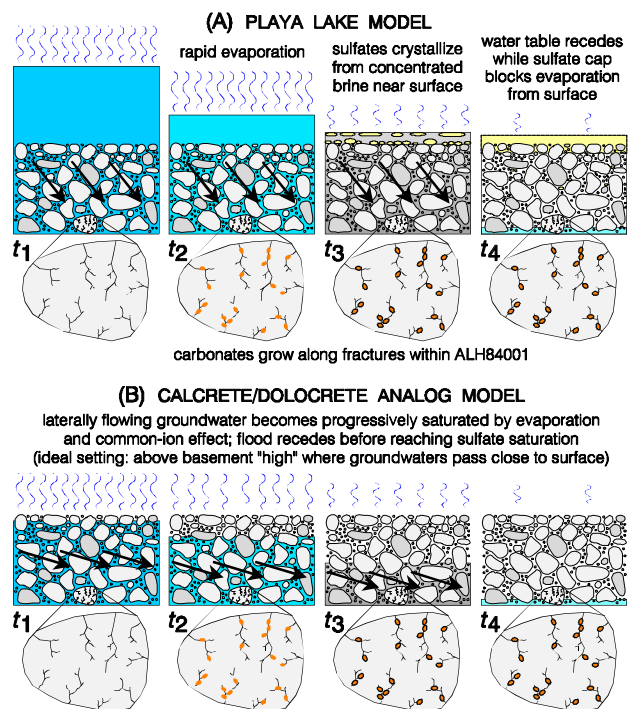
The popular hydrothermal model [3] is inconsistent with the virtual absence of secondary hydrated silicates in ALH84001. Prior brecciation should have facilitated aqueous alteration. Hydrothermal fluids would be at least warm, and rate of hydration of mafic silicates obeys an Arrhenius law, at least to ~100°C [4]. Most important, hydrothermal systems, and thus hydrothermal alteration episodes, tend to last for many years.

Many areas of Mars show evidence of infrequent but extensive flooding. I propose that the carbonates formed as evaporite deposits from floodwaters that percolated through the fractures of ALH84001, but only briefly, as evaporation and groundwater flow caused the water table to quickly recede beneath the level of this rock during the later stages of the flood episode. The setting might have been a layer of megaregolith debris (perhaps dumped from the flood) beneath a surface catchment of pooled floodwater, analogous to a playa lake. In this case, carbonate precipitation would occur in response to evaporative concentration of the pooled water (Figure). To explain the scarcity of sulfates in ALH84001, the water table must be assumed to recede quickly relative to the rate of evaporation. During the period when ALH84001 was above the water table,

evaporation would have slowed, as the evaporation front passed beneath the surface of the debris layer, and possibly earlier, if the shrinking pool of surface water developed a porous sulfate crust. Alternatively, ALH84001 may have developed as a martian form of calcrete, i.e., the evaporating flood(s) may have been entirely below ground as it (they) passed slowly through ALH84001. The greatest advantage of the flood evaporite model is that it exposes ALH84001 to carbonate precipitation without exposing it to prolonged aqueous alteration. The model also seems consistent with oxygen isotopic data: $\delta^{18}O$ increasing from +5 in the early, high-Ca/Mg carbonates to +25 in later carbonates [5], an evolution opposite to that implied by closed-system fluid-carbonate fractionation.

The flood evaporite hypothesis does not seem consistent with the suggestion [6] that the ALH84001 carbonates are biogenic. Martian floods were probably too infrequent to enable evolution of flood-dependent organisms. Conceivably, however, dead organisms or their appendages were fossilized by passive engulfment in the growing carbonates.

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(A) PLAYA LAKE MODEL

rapid evaporation — sulfates crystallize from concentrated brine near surface — water table recedes while sulfate cap blocks evaporation from surface

carbonates grow along fractures within ALH84001

(B) CALCRETE/DOLOCRETE ANALOG MODEL

laterally flowing groundwater becomes progressively saturated by evaporation and common-ion effect; flood recedes before reaching sulfate saturation (ideal setting: above basement "high" where groundwaters pass close to surface)

SHOCK EXPERIMENTS USING HOMESTAKE FORMATION AS AN ANALOG FOR THE CARBONATE IN METEORITE ALH 84001.

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Introduction: The origin of the carbonate within the meteorite ALH 84001 became an especially interesting petrologic puzzle since it was announced that the formation of carbonate involved biogenic processes on mars [1]. Alternative hypotheses for the formation of the carbonate have been presented [2–4], including the suggestion that the present carbonate occurrences crystallized from carbonate melt produced during impact on Mars [4]. As part of our experimental approach to examining mechanisms capable of forming and affecting carbonates similar to those in ALH 84001, we acquired samples of the Proterozoic (~1.9Ga) Homestake Formation (HF) for shock recovery experiments. The HF is a carbonate facies iron formation, most notable for its gold content. The HF is a good analog to ALH 84001 because it is a non-porous rock composed predominantly of siderite and ankerite, with minor quartz, orthoclase, albite, biotite, Fe-sulfides, rutile and Fe-oxides. The effects of shock on silicate rocks and minerals are well characterized [5] and serve as internal controls. Shock recovery experiments were conducted to pressures up to 65 GPa.

Experiments: Disks 7mm in diameter and 1mm thick were prepared from a sample of HF obtained from the U.S.G.S. The HF is very fine grained (<.5mm) and has an anhedral, granular texture. The rock is foliated with very fine scale laminations. Lighter colored lamina consist of interspersed siderite, ankerite, quartz, orthoclase, and albite. Darker lamina contain higher concentrations of anhedral interstitial biotite, sulfides, and oxides. The biotite is in various stages of the prograde reaction to orthoclase and Fe-oxide. The disks were prepared and shocked using a 20 mm powder propellant gun to accelerate flat flyer-plates [6]. Polished thin sections of the recovered coherent materials were prepared.

Results: Present data are from experiments at 0, 9.9, 31.2, 31.4, 31.5, 33.2, 34.4, 37.5, 39.3, and 51.2 GPa. The HF contains evidence of at least upper amphibolite facies regional metamorphism, as best expressed by the prograde conversion of biotite to or-thoclase and iron oxide. It is important to note that the carbonates in the zero sample demonstrate no adverse effects from the thermal metamorphic event. The 9.9 GPa experiment shows very little change from the zero control sample, however, in the 31.2 GPa experiment biotite has started to decompose. Optically it is dark brown to black and opaque and in back-scattered electron imagery it is vesicluated and frothy. The carbonates perhaps show some mild additional fracturing, but they are not planar deformation features. In the 34.4 GPa experiment, the quartz and feldspar components have become isotropic, a higher percentage of the biotite has decomposed, and the carbonate is still relatively unaffected. The carbonate in the 39.3 GPa experiment shows some apparent decomposition to oxide, similar to the static pressure experiments of [7]. Most of the biotite has decomposed in the 51.2 GPa experiment. The carbonate shows more decomposition to oxide, but there is no evidence of carbonate melting. Two more experiments up to 65 GPa are in progress, but appear unlikely to produce carbonate melts.

Conclusions: We were unable to produce carbonate melts at pressures as high as 51 GPa, consistent with others [e.g. 8]. It is unlikely that the carbonate in the meteorite ALH 84001 has crystallized from shock produced melts.

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FORMATION OF PRE-IMPACT, INTERSTITIAL CARBONATES IN THE ALH84001 MARTIAN METEORITE.

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We have argued that the existing carbonates in fractures in ALH84001 were derived from impact melts [1,2]. The morphology and distribution of carbonate and plagioclase glass in the fracture zones precludes formation of the existing carbonates in vugs or by replacement of plagioclase glass. We infer that carbonates in fractures and fracture zones were derived from preexisting carbonates that were located at interstitial sites closely associated with plagioclase, along with minor chromite and traces of silica, phosphate and orthoclase. Since plagioclase was entirely melted by shock [3], the adjacent phases must have experienced high post-shock temperatures and shock pressures of ~40 GPa. Thus impact may have drastically changed the abundance and composition of the interstitial minerals in ALH84001: for example, carbonates, sulfates, and clay minerals may have partly decomposed, as in shergottites, which are also heavily shocked [4]. In ALH84001, magnetites probably formed during impact by partial decomposition of siderite [5] and trace amounts of olivine appear to have formed around carbonate nodules [6] in fractures. However, the relatively small amounts of olivine and magnetite suggest that these reactions did not cause drastic changes in the major-element bulk composition of the carbonate.

We consider four possible origins for the interstitial carbonates that we infer to have existed in ALH84001 prior to impact; 1) crystallization from residual igneous melts, 2) reaction of plagioclase with metasomatic magmatic fluids that percolated along grain boundaries, 3) hydrothermal replacement of plagioclase, and 4) low-temperature precipitation from aqueous solutions in vugs. All four models have problems. High temperature formation would account for the similarity in mean Mg/(Mg+Fe) of carbonates and pyroxene, and might be favored by the similarity of $\delta^{18}O$ of pyroxene and dolomite [7]. However, the difference in $\Delta^{17}O$ between carbonate and Martian meteorite whole rock values [8] shows that the existing carbonates could not have formed from a purely magmatic source and must have formed from a source that acquired an atmospheric O component. This favors a near surface origin for the pre-existing carbonates though the atmospheric component could have been acquired by magmatic carbonates during impact. Another argument against a magmatic origin is the high pressure required to prevent carbonate and pyroxene from reacting to form CO_2: at 900 °C pressures of >1.5 GPa and burial depths of ~120 km would be needed [9]. Excavation of ALH84001 from such depths after cooling seems less plausible. The probable existence of Martian atmosphere in ALH84001 [10] appears to require a near-surface location at the time of shock melting.

Although most authors favor a low-temperature origin for the carbonates and salts in other Martian meteorites [4], high-temperature processes have also been proposed for Zagami [11] and Nakhla [12]. Low-temperature formation as evaporite deposits [13, 14] would be consistent with evidence for episodic and brief infiltrations of water in Lafayette [15] and Chassigny [16], the absence or lack of silicate alteration in Martian meteorites [4, 14-16], and photogeologic evidence for episodic flows of water on Mars, even on recent lava flows [17].

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GEOCHEMISTRY OF CARBONATES AND GLASS IN ALH84001. J. M. Eiler[1], J. W. Valley[2], C. M. Graham[3], and J. Fournelle[2], [1]Geological and Planetary Sciences, California Institue of Technology, Pasadena CA 91125 (eiler@gps.caltech.edu), [2]Geology and Geophysics, University of Wisconsin, Madison WI 53706, [3]Geology and Geophysics, University of Edinburgh, Edinburgh Scotland, United Kingdom.

The stable isotope geochemistry of carbonates in SNC meteorites constrains both the characteristics of martian volatile reservoirs and the origin of secondary mineralization in these samples. We report here new ion microprobe measurements of $^{18}O/^{16}O$ in carbonates and related phases in ALH84001, supported with major-, minor-, and trace-element data on the same materials.

The background to these measurements is that carbonates in ALH84001 display a large range in oxygen isotope composition (~25‰; [1–4]), which has been ascribed either to variations in temperature [1,3,5] or Rayleigh distillation [4]. When examined in detail, variations in oxygen isotope ratio in carbonates have been shown to be correlated systematically with variations in their major element composition [1,3,4]. Although the data from several different groups are generally consistent, one difference is that ankeritic carbonates (~50% $CaCO_3$) were reported by [3] to have $\delta^{18}O_{SMOW}$ 0‰, but [4] found values of ~7‰ for carbonates in this compositional range.

We have made 82 measurements of $\delta^{18}O$ in carbonates from ALH84001, including a range of ankeritic compositions not encountered in previous studies and ~20 measurements each of all of the major populations/textural types of carbonate known in this sample. Our results confirm the overall trend of $\delta^{18}O$ with chemical composition seen in previous studies [1–4]: i.e., $\delta^{18}O$ varies by ~25‰ and tends to decrease with increasing Ca content. However, our data reveal details in the correlations between $\delta^{18}O$ and chemistry not observed in previous, smaller data sets. In particular, two distinct, offset trends occur in plots of $\delta^{18}O$ vs. major elements: (1) decreasing $\delta^{18}O$ (26→0‰) with decreasing Mg and increasing Ca and Mn in white magnesites and orange magnesio-siderites, and (2) ankerites having a large range in chemical composition (0.45 ≤ X_{Ca} ≤ 0.71) with essentially indistinguishable $\delta^{18}O$ values (5.8 ± 1.9‰). There may be a subtle discontinuity in $\delta^{18}O$ and chemical composition on the first trend, between magnesites (0.70 ≤ X_{Mg} ≤ 0.90; X_{Ca} ≤ 0.05) and magnesio-siderites (X_{mg} < 0.70; 0.08 ≤ X_{Ca} ≤ 0.44). Our results for ankeritic carbonates are within analytical uncertainty of [4] and in disagreement with [3]. These two trends are associated with distinct carbonate textures: magnesites and magnesio-siderites are found principally in concentrically zoned "disks" [6] and ankerites exclusively found in irregularly shaped patches.

Mn concentration is strongly correlated with Ca in ALH84001 carbonates. There are again two distinct trends, one for magnesites and magnesio-siderites and one for ankeritic carbonates, offset from each other in Ca/Mn ratio. On average, the ankerites also have higher La/Nd and Sr/Ba ratios, higher Sr and Y concentrations, and lower Ba concentrations than magnesites and magnesio-siderites. $\delta^{18}O$ is negatively correlated with La/Nd and Sr/Ba among all analyses. On average, magnesites have higher La/Y ratios and Th concentrations than other carbonate populations. All populations of carbonate have LREE-depleted rare earth patterns relative to coexisting feldspathic glass (see also [7]).

Differences in REE abundances between carbonates and feldspathic glasses are not those predicted by carbonate/silicate-melt distribution coefficients, and therefore no population of carbonate considered in this study can be consanguineous with melt from which much of the glass in ALH84001 appears to have quenched. REE and other trace element abundances vary systematically with crystallization sequence (e.g., decreasing La/Nd from ankerite→magnesio-siderite→magnesite). These variations are in the opposite direction of those predicted by fractional precipitation from a carbonic fluid based on known carbonate/fluid distribution coefficients. Given correlations between $\delta^{18}O$ and chemistry, models in which variation in $\delta^{18}O$ is due to precipitation over a range of temperatures require complex variation of fluid/carbonate distribution coefficients with temperature. Alternatively, carbonate may have precipitated from at least two chemically and isotopically distinct fluids, such that correlations among $\delta^{18}O$ and chemistry reflect different mixing proportions of end-member fluid compositions.

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HYDROGEN ISOTOPE STUDIES OF CARBONATE AND PHOSPHATE IN MARTIAN METEORITE

ALH84001; N. Z. Boctor[1], J. Wang[2], C. M. O'D Alexander[2], E. Hauri[2], C. M. Bertka[1], and Y. Fei[1], [1]Geophysical Laboratory, Carnegie Institution of Washington, 5241 Broad Branch Rd., NW, Washington, DC 20015; [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., NW, Washington, DC 20015.

Carbonate and phosphate minerals in ALH84001 are minor but significant constituents. Previous investigations [1–6] were concerned with the origin of the carbonates, their O and C isotope compositions, and their potential as biomarkers of ancient life on Mars. Phosphate minerals received less attention than carbonates. Because whole rock hydrogen isotope data on ALH84001 [7] indicate the presence of a high temperature hydrogen component, we investigated the hydrogen isotopic composition of the carbonate and whitlockite in this meteorite [8]. In view of the low δD values of whitlockite and carbonate relative to the whole rock, there was concern that epoxy contamination may have contributed to the measurements. In this investigation, we report additional ion microprobe analysis of the carbonate and whitlockite in ALH84001. We measured the C/H ratio on the epoxy and on the minerals and corrected the δD values for any possible contribution of the epoxy. To maximize the correction, we assumed that all carbon counts in whitlockite analyses are derived from epoxy. The analyses were performed at 12.5KV with oxygen primary beam of 2nA. The analyzed area was ~5 to 25 μm, and an amphibole standard was used. Based on the H count rates measured in two amphibole standards, and assuming that all H (after epoxy correction) in the samples is present as water, we have estimated the water contents of the whitlockite and carbonate. The results are given in table 1 and are compared to our previous analyses using a Cs primary beam.

The δD values of whitlockite from ALH84001 are much lower than those reported by (9) from Zagami (δD + 4000‰) which reacted with crustal waters that equilibrated with the Martian atmosphere. They are also lower than the δD values (~ +1680 to +3570 ‰) in apatite from the shergottite QUE94201 (10). There also is a positive correlation between δD and water contents of the whitlockite and carbonate, contrary to what was observed by (10) in apatite from the shergottite QUE94201. The δD values of the carbonate and whitlockite show that there is an extraterrestrial hydrogen component in ALH84001. The report by (11) of phyllosilicates in ALH84001 adds credence to the notion that extraterrestrial water was present in this meteorite. This is consistent with the presence of a high temperature hydrogen in the whole rock (δD + 800‰) reported by (7). Because there is a low temperature terrestrial hydrogen component released during stepwise heating of ALH84001 whole rock (7), it is possible that there is also a terrestrial component to our measurements of whitlockite and carbonate and that the indigenous δD of whitlockite and carbonate are heavier. The δD of +800 ‰ of the whole rock high temperature hydrogen constrains the upper limit of the δD of whitlockite and carbonate; however, diffusive fractionation of D/H ratios during stepped heating may also bias the whole rock δD to high values. If the hydrogen component in ALH84001 is magmatic, this would imply that hydrous magma with a low activity of water may have existed in the Martian mantle ~ 4.5 Gyr ago. Alternatively, the hydrogen signature may represent an interaction of ALH84001 with crustal fluids that equilibrated with a primitive atmosphere that was much less fractionated than the present day Martian atmosphere.

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Table 1. Ion Probe Analyses of Hydrogen Isotopes of Whitlockite and Carbonate in ALH 84001

Mineral Beam	O Beam			Cs
	δD ‰	δD_{Corr}* ‰	Water ppm	δD ‰
Whitlockite	+477±17	+500	1600	+287±12
	+270±22	+280	1100	+216±12
	+166±20	+181	800	+201±14
Carbonate	+209±22		700	+313±5
	+175±23		400	+185±10
				+165±11

* Corrected for possible contribution from epoxy.

BEAGLE 2: A LANDER FOR MARS. C. T. Pillinger[1] and M. R. Sims[2] on behalf of the Beagle 2 Consortium, [1]Planetary Science Research Institute, Open University, Milton Keynes, MK7 6AA, UK, [2]Space Research Centre, Department of Physics and Astronomy, University of Leicester, University Road, Leicester, LE1 7RH, UK.

The year 2003 sees an opportunity for Europe to have its own planetary mission to Mars.

The aim of the Beagle 2 project is to address each of the five objectives set out by the Science Definition Team for landers on the Mars Express Mission. Thus Beagle 2 seeks a full geological, mineralogical and geochemical investigation programme to characterise a landing site likely to have experienced erosion by water transport mechanisms with an altitude less than +2km with respect to the martian datum. The geochemical approach will include a qualitative, quantitative and isotopic inventory of the light elements, H, C, N, O and S in their "organic", inorganic and atmospheric situations. The distribution of the elements between species and any observed isotopic fractionation is to be used as a guide to provenance. In this respect, since recent work with martian meteorites indicates the existence of low temperature geochemistry on Mars, a major aim will concern Exobiology, to establish whether (i) conditions appropriate to life prevail, (ii) any evidence for past life has survived or (iii) global disequilibrium, consistent with an active biology, exists. Because of the presumed harsh oxidising conditions at the surface to atmospheric interface on Mars, materials selected from protected sites (subsurface or rock interiors) must comprise the major source of data. In any event, this deleterious property of the planet must be investigated for the benefit of future mission. The samples subjected to light element analysis will be scrutinised by close up imagery, documented in terms of chemical make up/mineralogy and hopefully age dated. The selection of appropriate materials for study requires surface mobility of a rover/retriever and deployment of a burrowing device/mole and a rock chipper/corer. To accord with the aspirations of groups wishing to investigate the internal structure and climate of Mars, Beagle 2 lander provides a geophysical station.

At the focus of the Beagle 2 instrument package, and integrated with the Lander, will be a mass spectrometer with a detector system compatible with a variety of modes of operation. It will be employed in conjunction with a chemical processing system designed to deliver species in a form fit for analysis, at high sensitivity and precision levels, including isotopic measurements. To survey the site, the Lander will have a multispectral panoramic camera. The tethered Rover camera navigated, with a range of 10-20 metres, will be capable of retrieving samples from undisturbed soils beneath boulders and subsurface and samples from boulders following the removal of the weathered outer layers. The Rover will interface with a sample handling/extraction system and also be able to deploy an APX and Mössbauer spectrometer sensor as well as a microscope against the cleaned rock surfaces. The complete instrument package requires 20kg and <20watt which will be provided by the Beagle 2 lander systems, the probe having been delivered to the surface of Mars according to principles similar to those employed by the NASA Pathfinder mission. Data from the instruments will be relayed via the Lander and Orbiter back to Earth. All instruments proposed for Beagle 2 are either already developed or in an advanced stage of development.

The total mass of the Probe and Orbiter attached subsystems is less than 11.3kg (including contingency and the Orbiter based transponder system). The probe will be spin ejected from the Orbiter up to 12 days prior to arrival at Mars and enter and land using an aeroshell, parachute, retro-rocket and airbag system. The Lander will self-right itself and deploy solar panels for power. Following initial status checks via the ground system, the Rover will be deployed to fulfill the geochemistry and exobiological investigations. Geophysical data from the on-board meteorological instruments, seismometer and magnetometer will be collected in parallel. The Lander will have a nominal lifetime of 1 martian year on the surface.

The Beagle 2 Probe is proposed by a consortium of institutions and European industry.